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The SIT Model Parameters for Interactions of Uranyl Ion with Chloride and Nitrate Ions

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Abstract
The SIT model for activity coefficients of aqueous ions is popular among radiochemists. So far, this model has no parameters for interactions between uranyl ion and the chloride and nitrate anions, as their evaluation from activity coefficients of uranyl chloride and nitrate could not be recommended due to partial association of these electrolytes. This study discusses the relations of the thermodynamics of associated electrolytes that allows correction of the activity coefficients for effects of complex formation and thus determine the "true" values of the SIT interaction coefficients. At 298 K the following values are obtained: $\epsilon\left(UO_2^{2+}, Cl^-\right) = (0.32 \pm 0.03)$; $\epsilon\left(UO_2Cl^+, Cl^-\right) = (0.32 \pm 0.02)$; $\epsilon\left(UO_2^{2+}, NO_3^-\right) = (0.28 \pm 0.02)$; $\epsilon\left(UO_2NO_3^+, NO_3^-\right) = (0.34 \pm 0.02)$.

Keywords Activity coefficients · The SIT model · Uranyl-chloride interaction coefficient · Uranyl-nitrate interaction coefficient

1 Introduction

The assessment and optimization of safety of nuclear waste repositories in deep geological formations includes thermodynamic modeling of radionuclide transport with calculation of phase equilibria and concentrations of aqueous species [1, 2]. Reliability of such modeling depends heavily on quality and comprehensiveness of thermodynamic data (such as the Gibbs energy of solid phases and aqueous species in their standard state of infinite dilution in water and the parameters of the model for activity coefficients). For over 100 years compilations of thermodynamic properties have been published [3–8]. However, in the absence of the commonly accepted values of the thermodynamic functions of key compounds the results of different compilations generally cannot be freely combined. In 1989, an important milestone was achieved with the publication by CODATA (Committee on Data for Science and Technology) of recommendations for key values for thermodynamics [9]. The OECD Nuclear Energy Agency Thermochemical Database (NEA-TDB) project, accepting the CODATA values for key

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compounds as a basis, for over the past 30 years significantly increased the number of solid phases and aqueous species, for which internally consistent and quality assured thermodynamic properties at 298.15 K and 0.1 MPa are tabulated in 15 already published volumes, the last of which currently is the update on thermodynamic properties of U, Np, Pu, Am and Tc [10]. A distinguished feature of NEA-TDB compilations is the review of sources considered with the detailed discussion of data selection and recommendations. Generally, the state-of-the-art with the availability of the standard-state (i.e., referenced to infinite dilution in water) thermodynamic properties of aqueous species can be termed satisfactory.

In order to calculate the Gibbs energies of aqueous species (or values of equilibrium constants) at finite concentrations, it is necessary to know activity coefficients, γ, of these species in water. Pitzer's model [11] is most popular for calculation of γ. In most cases, three concentration parameters are necessary for each electrolyte, MX, in Pitzer's model ($\beta^{(o)}_{MX}$, $\beta^{(1)}_{MX}$, and C^{φ}_{MX}), with additional mixing parameters required for mixtures of salts (θ for each unlike cation–cation or anion–anion pair and ψ for triple combinations of ions). This model allows a very precise reproduction of the surfaces of chemical potentials of aqueous mixtures. However, complex formation is usually ignored in this model. The reason is a large increase in the number of required Pitzer parameters when explicitly considering complexation. For example, for aqueous UO_2Cl_2 solutions 3 Pitzer parameters ($\beta^{(o)}_{UO_2,Cl}$, $\beta^{(1)}_{UO_2,Cl}$, and $C^{\varphi}_{UO_2,Cl}$) allow for precise reproduction of stoichiometric mean ionic activity coefficients, $\gamma_{\pm}$, available at molalities from 0.1 to 2.0 mol·kg^{-1} [12]. On the other hand, solution chemists are aware of the formation of at least one complex species, UO_2Cl^+, in aqueous solutions of uranyl chloride, see the corresponding discussion in a recent NEA-TDB review [10]. However, the inclusion of this complex in the thermodynamic description of the UO_2Cl_2–H_2O system requires the determination of additional Pitzer parameters $\beta^{(o)}_{UO_2Cl,Cl}$, $\beta^{(1)}_{UO_2Cl,Cl}$, $C^{\varphi}_{UO_2Cl,Cl}$, θ_{UO_2Cl,UO_2} and $\psi_{UO_2Cl,UO_2,Cl}$, thus increasing the total number of fitting parameters from three to eight. The meaningful determination of 8 fitting parameters from a limited number of $\gamma_{\pm}$ data points (15 in total) is hardly possible.

This is probably one of the reasons why the NEA-TDB project adopted a simpler model for activity coefficients of ions in water, the so-called SIT model. This model was outlined by Ciavatta [13] in 1980, based on theoretical considerations of Brønsted [14], Guggenheim [15, 16] and Scatchard [17, 18]. In the SIT model, the relation for the activity coefficient of a cation, γ_c, of a charge z_c is given by

$$\log_{10}\gamma_c = -z_c^2 D + \sum_a \epsilon(c,a) m_a, \tag{1}$$

where the Debye–Hückel term D in the SIT model is given by

$$D = \frac{A I^{0.5}}{1 + 1.5 I^{0.5}}, \tag{2}$$

where $A = 0.510$ kg$^{0.5}$·mol$^{-0.5}$ is the limiting Debye–Hückel slope for the decadic logarithm of the activity coefficient; I is the ionic strength ($I = 0.5 \sum_i m_i z_i^2$), the index i covers all the ions in a solution; $\epsilon(c,a)$ is the SIT cation–anion binary interaction coefficient between a cation c and an anion a. The corresponding equation for an anion a is obtained by interchanging a for c. The SIT coefficients have a dimension of kg·mol^{-1}, later in the text the dimensions will be omitted for brevity.

For electrolytes, the stoichiometric mean ionic activity coefficients, $\gamma_{\pm}$, are tabulated in handbooks. We recall that for an electrolyte $M_{\nu_M}X_{\nu_X}$ the following definition is held

$$\gamma_{\pm}^{\nu} = \gamma_M{}^{\nu_M}\gamma_X{}^{\nu_X}, \tag{3}$$

where $\nu = \nu_M + \nu_X$. In this case the word "stoichiometric" means that the electrolyte is considered to be fully dissociated. The SIT model gives the following expression for $\gamma_{\pm}$ of the $M_{\nu_M}X_{\nu_X}$ salt [13, 19, 20]:

$$\log_{10}\gamma_{\pm} = -|Z_M Z_X|D + \frac{2\nu_M\nu_X}{\nu}\epsilon(M,X)m. \tag{4}$$

Another property that will be considered is the osmotic coefficient of a solution, ϕ, that in the thermodynamics of electrolytes is a traditional measure of the water activity, a_w, in a solution of s single electrolyte:

$$\phi = -\frac{N_w}{\nu m}\ln a_w, \tag{5}$$

where $N_w \approx 55.5084$ is the number of moles of H_2O in 1 kg of water. Osmotic coefficients are usually obtained from the isopiestic measurements, where the studied solution is equilibrated with a reference (a solution of a well-studied electrolyte), for which the water activity as a function of concentration is known with high precision [21]. The SIT model gives the following expression for the concentration dependence of osmotic coefficients [13, 19] of an electrolyte $M_{\nu_M}X_{\nu_X}$:

$$\phi - 1 = -\frac{|Z_M Z_X|A\ln 10}{(1.5)^3 I}\left(t - 2\ln t - \frac{1}{t}\right) + \frac{\nu_M\nu_X}{\nu}\varepsilon(M,X)\ln 10 \cdot m, \tag{6}$$

where

$$t = 1 + 1.5I^{0.5}. \tag{7}$$

The difference between the SIT and Pitzer's model is that the SIT approximation ignores all ternary (triple) ion interactions, the like-sign interactions and considers the interaction coefficients to be constant (i.e., it ignores ionic strength dependence of the second virial coefficients). As a result, the SIT is significantly less precise in reproduction of the mean ionic activity coefficients. For example, the uncertainty σ for the fit of 15 data points for the natural logarithms of the UO_2Cl_2 activity coefficients [12] at molalities 0.1–2.0 mol·kg^{-1} by Pitzer's model is 0.0013 (the maximum error in $\gamma_{\pm}$ is ~0.2%), while it is 0.028 for the fit by the SIT model (the maximum error is about 4.8%). Nevertheless, as the main area of use of the SIT is the correlation of the concentration dependences of equilibrium constants of complex formation equilibria, which often have uncertainties of 0.1 $\log_{10}$ unit (20–25%) and even more, the intrinsic precision of the SIT model is sufficient for correlating such data. Currently, there are more than 400 binary interaction coefficients in the NEA-TDB project database, most of which include complex species.

Despite multiyear efforts, there are still disappointing gaps in the collection of the SIT interaction coefficients $\epsilon(c,a)$. For example, for the key uranium aqueous species UO_2^{2+} the following results are given in the 2020 NEA volume [10]: $\epsilon\left(UO_2^{2+}, Cl^-\right) = (0.21 \pm 0.02)$, $\epsilon\left(UO_2^{2+}, ClO_4^-\right) = (0.46 \pm 0.03)$ and $\epsilon\left(UO_2^{2+}, NO_3^-\right) = (0.24 \pm 0.03)$, all "reported by Ciavatta [13]" with a comment "These coefficients were not used in [22] because they were

evaluated by Ciavatta [13] without taking chloride and nitrate complexation into account. Instead, Grenthe et al. [22] used $\epsilon\left(UO_2^{2+}, X\right) = (0.46 \pm 0.03)$ kg·mol^{-1}, for X = Cl^-, ClO_4^- and NO_3^-". Indeed, complexation decreases the mean ionic activity coefficients of an associated electrolyte compared to the situation of its full dissociation [12], so, the evaluated in this way interaction coefficients will be smaller than "true" ones. However, the approximation of equality of the SIT interaction coefficients between UO_2^{2+} and Cl^-, ClO_4^- and NO_3^- cannot be recommended, as the simple theory of interionic interactions shows that the binary interaction coefficient depends primarily (but not exclusively) on the sizes of a cation and an anion [11, 23]. Sizes of Cl^-, ClO_4^- and NO_3^- vary significantly, as can be deduced from the values of the partial molar volumes of these ions in water at 298.15 K and 0.1 MPa: 17.83, 44.34, 29.21 cm^3·mol^{-1}, respectively [24].

Briefly, there is a common understanding that the evaluation of the SIT interaction coefficients from the mean ionic activity coefficients of partially associated electrolytes should not be performed. As a result, most recommended $\epsilon(c, a)$ include perchlorate as an anion, because perchlorate salts are known to be far less associated compared to chlorides and particularly nitrates. For historical reasons most values of stability constants are reported for perchlorate media, so, $\epsilon\left(c, ClO_4^-\right)$ are valuable for extrapolation of equilibrium constants to infinite dilution. Nevertheless, for technological applications interactions with chloride and nitrate anions are required more often than those with ClO_4^-. Returning to UO_2^{2+}, currently one may accept that $\epsilon\left(UO_2^{2+}, ClO_4^-\right) = (0.46 \pm 0.03)$ (no significant UO_2^{2+} –ClO_4^- complex formation), while for interactions with the chloride and nitrate ions only the lower bounds can be specified, that were evaluated from $\gamma_\pm$ assuming (wrongfully) no association: $\epsilon\left(UO_2^{2+}, Cl^-\right) > 0.21$ and $\epsilon\left(UO_2^{2+}, NO_3^-\right) > 0.24$.

However, the use of relations following from the thermodynamics of associated electrolytes [12, 25] offers a way of calculation of $\epsilon\left(UO_2^{2+}, Cl^-\right)$ and $\epsilon\left(UO_2^{2+}, NO_3^-\right)$ from stoichiometric mean ionic activity coefficients explicitly accounting for association of uranyl ion with chloride and nitrate anions, as will be shown in this study.

2 Thermodynamic Background

2.1 Basic Relations

As was already noted, handbooks tabulate the mean ionic activity coefficients, $\gamma_\pm$, that are calculated from experimental data assuming that electrolytes are fully dissociated (the so-called mean ionic stoichiometric activity coefficients). On the other hand, solution chemists are well aware that many electrolytes are partially associated. This issue is well recognized in the SIT community and it is understood that many ϵ values, evaluated from the stoichiometric mean ionic activity coefficients, implicitly include effects of association of an electrolyte. The question arises – how to take into account the association and remove its effects from the tabulated $\gamma_\pm$ values. For that, one has to know the so-called "true" ionic activity coefficients of a cation, γ'_M, and of an anion, γ'_X, and their relation to stoichiometric counterparts. The principal result of the so-called "equilibrium model" of solutions of an associated $M_{\nu_M}X_{\nu_X}$ electrolyte is the relation [12], [25]

$$(\gamma_M m_M)^{\nu_M}(\gamma_X m_X)^{\nu_X} = \left(\gamma'_M m'_M\right)^{\nu_M}(\gamma'_X m'_X)^{\nu_X}, \tag{8}$$

where m'_M and m'_X are equilibrium molalities of a cation and an anion (for example, equilibrium molalities of UO_2^{2+} and Cl^- in aqueous UO_2Cl_2 solutions, where UO_2^{2+} and Cl^- coexist with chloride complexes of uranyl ion). As discussed in the literature by Robinson and Stokes [12] and Goldberg [25], this relation follows from the principle that the chemical potential of an ion is independent of any presentation of it.

For aqueous UO_2Cl_2 and $UO_2(NO_3)_2$ the primary source of experimental activity data is the study by Robinson and Lim [26], which reports stoichiometric osmotic coefficients ϕ, i.e., calculated with Eq. 5 assuming the full dissociation of uranyl salts. For a partially associated electrolyte the term νm in the denominator of Eq. 5 should be replaced with $\sum_i m_i$, i.e., the total number of species present in a solution. As the water activity in a solution is independent of our representation of speciation of a dissolved electrolyte, one obtains the relation between stoichiometric, ϕ, and "true", ϕ', osmotic coefficients of a solution:

$$\phi = \phi' \frac{\sum_i m_i}{\nu m}. \tag{9}$$

Equations 8 and 9 are the principal relations of the "equilibrium model" for presentation of activities of associated electrolytes. They have been employed, usually without comments, when treating activity of compounds of associated electrolytes, often acids, such as hydrofluoric, sulfuric and phosphoric acids, within "equilibrium models" [25, 27–30, and others].

2.2 A Practical Case of a Single Complex Formed in a Solution

From a practical point of view, the most important is the case of formation of a single complex species in a solution, otherwise the necessity to determine several interaction parameters and equilibrium constants will strongly complicate efforts and may result in an ill-conditioned problem. This particular question was analyzed more than 60 years ago in the well-known book of Robinson and Stokes [12]. These authors solved in a general analytical form the connection between the stoichiometric and "true" activity coefficients for an important case of formation of just one complex in a solution. They derived the following relation between $\gamma_\pm$ and $\gamma'_\pm$ for the case of an electrolyte $M_{\nu_M}X_{\nu_X}$, when a single complex of a composition $M_{n_1}X_{n_2}$ forms:

$$\gamma_\pm^\nu = \alpha^{\nu_M}\left[1-(1-\alpha)\frac{n_2\nu_M}{n_1\nu_X}\right]^{\nu_X}\left(\gamma'_\pm\right)^\nu, \tag{10}$$

where as before $\nu = \nu_M + \nu_X$; α is a share of a "free" (uncomplexed) cation. Similarly, one can obtain the closed analytical relation between the stoichiometric, ϕ, and "true", ϕ', osmotic coefficients, again for the case of a single complex formation:

$$\phi = \frac{\phi'}{\nu}\left[\alpha\nu_M + (1-\alpha)\frac{\nu_M}{n_1}\left(1-n_2\right) + \nu_X\right]. \tag{11}$$

We expect, that a combination of Eq. 10 or 11 with the SIT model will allow determination of the SIT coefficients (corrected for partial association) for both an electrolyte $M_{\nu_M}X_{\nu_X}$ and for an ionic pair $M_{n_1}X_{n_2}$ together with the (usually known) stability constant at infinite dilution for this ionic pair.

3 Results for Uranyl Chloride and Nitrate

3.1 The Case of Uranyl Chloride

3.1.1 Chloride Complex Formation in Aqueous UO_2Cl_2 Solutions

The uranyl chloride complexes are weak. However, their existence follows not only from the formal interpretation of spectrophotometric, emf, distribution, etc. results, but also from structure determinations in aqueous solutions by X-ray methods [31–33]. These studies reveal the formation of up to 3 chloride complexes in solutions with a large excess of Cl^- over the total uranyl concentration, when the $[Cl]/[UO_2]$ ratio in these studies changed from 5 to 900. At 1 mol·dm^{-3} Cl^- the average Cl^- coordination number varies from 0.3 [31] to 1.0 [33], and at 6 mol·dm^{-3} Cl^- the average Cl^- coordination number is calculated to be 1.5 [31], 2.3 [32] or 2.6 [33], the latter value refers to 6 mol·kg^{-1} Cl^-. Obviously, results are not very precise.

No quantitative speciation data are available for the binary UO_2Cl_2–H_2O system, where the $[Cl]/[UO_2]$ ratio is equal to 2, i.e., significantly smaller than in studies mentioned above, thus demoting the complex formation. So, we expect based on available data that the second and third chloride complexes appear in significant amounts only in brines at high Cl^- concentrations, and at UO_2Cl_2 molalities below ~1.5 mol kg^{-1} the first chloride complex UO_2Cl^+ dominates absolutely. The principal complex formation reaction is

$$UO_2^{2+} + Cl^- \overset{K}{\rightleftharpoons} UO_2Cl^+. \tag{12}$$

3.1.2 Thermodynamic Relations Specific for UO_2Cl_2 Solutions with the Formation of a Single UO_2Cl^+ Complex

The Robinson-Stokes relation, Eq. 10, for this case ($\nu_M = 1$, $\nu_X = 2$, $n_1 = 1$, $n_2 = 1$) should be written as

$$\gamma_\pm^3 = \frac{\alpha}{4}[1+\alpha]^2\left(\gamma'_\pm\right)^3, \tag{13}$$

or

$$\log_{10}\gamma_\pm = \log_{10}\gamma'_\pm + \frac{1}{3}\left\{\log_{10}\frac{\alpha}{4} + 2\log_{10}(1+\alpha)\right\}, \tag{14}$$

where α is the share of the free UO_2^{2+}.

Under assumptions made, the following species are present in a solution: UO_2^{2+}, UO_2Cl^+ and Cl^-. Their concentrations are given by

$$m_{UO_2^{2+}} = \alpha m, \tag{15}$$

$$m_{UO_2Cl^+} = (1-\alpha)m, \tag{16}$$

$$m_{Cl^-} = (1+\alpha)m, \tag{17}$$

where m is the total (analytical) molality of uranyl chloride. The ionic strength, I, of a solution is

$$I = m(1 + 2\alpha). \tag{18}$$

For the "true" mean ionic activity coefficients, $\gamma'_{\pm}$, of UO_2Cl_2 one writes an analog of Eq. 3

$$\left(\gamma'_{\pm}\right)^3 = \gamma'_{UO_2^{2+}}(\gamma'_{Cl^-})^2. \tag{19}$$

In the framework of the SIT model, the following expressions are valid for the "true" activity coefficients of the species present in solution

$$\log_{10}\gamma'_{UO_2^{2+}} = -(z_{UO_2^{2+}})^2 D + \epsilon\left(UO_2^{2+}, Cl^-\right)m_{Cl^-} = -4D + \epsilon\left(UO_2^{2+}, Cl^-\right)(1+\alpha)m \tag{20}$$

$$\log_{10}\gamma'_{UO_2Cl^+} = -(z_{UO_2Cl^+})^2 D + \epsilon\left(UO_2Cl^+, Cl^-\right)m_{Cl^-} = -D + \epsilon\left(UO_2Cl^+, Cl^-\right)(1+\alpha)m \tag{21}$$

$$\begin{aligned}\log_{10}\gamma'_{Cl^-} &= -(z_{Cl^-})^2 D + \epsilon\left(UO_2^{2+}, Cl^-\right)m_{UO_2^{2+}} + \epsilon\left(UO_2Cl^+, Cl^-\right)m_{UO_2Cl^+} \\ &= -D + \epsilon\left(UO_2^{2+}, Cl^-\right)\alpha m + \epsilon\left(UO_2Cl^+, Cl^-\right)(1-\alpha)m.\end{aligned} \tag{22}$$

The extended form of the Robinson–Stokes relation is now

$$\log_{10}\gamma_{\pm} = -2D + \epsilon\left(UO_2^{2+}, Cl^-\right)(1+3\alpha)m + 2\epsilon(UO_2Cl^+, Cl^-)(1-\alpha)m + \frac{1}{3}\left\{\log_{10}\frac{\alpha}{4} + 2\log_{10}(1+\alpha)\right\}. \tag{23}$$

In addition, we need an expression for the stability constant, β_1^0, of UO_2Cl^+

$$\log_{10}\beta_1^0 = \log_{10}\frac{m_{UO_2Cl^+}}{m_{UO_2^{2+}}m_{Cl^-}}\frac{\gamma'_{UO_2Cl^+}}{\gamma'_{UO_2^{2+}}\gamma'_{Cl^-}} = \log_{10}\frac{(1-\alpha)}{\alpha m(1+\alpha)} + 2D - \epsilon\left(UO_2^{2+}, Cl^-\right)(1+2\alpha)m + 2\epsilon(UO_2Cl^+, Cl^-)\alpha m. \tag{24}$$

Next, we consider similar relations for the osmotic coefficients of UO_2Cl_2 solutions. First, Eq. 9 reduces to

$$\phi = \phi'\frac{2+\alpha}{3}. \tag{25}$$

For a mixture of ions, the SIT model gives the following expression for the osmotic coefficient of a solution [19, 20]

$$(\phi - 1)\sum_i m_i = -\frac{2A\ln 10}{(1.5)^3}\left(t - 2\ln t - \frac{1}{t}\right) + \sum_c\sum_a \epsilon(c,a)(\ln 10)m_c m_a, \tag{26}$$

where the double summation covers all cations and anions. This relation, when used for the "true" osmotic coefficient of UO_2Cl_2 solutions, reduces to

$$\begin{aligned}(\phi'-1)m(2+\alpha) = &-\frac{2A\ln 10}{(1.5)^3}\left(t - 2\ln t - \frac{1}{t}\right) + \epsilon\left(UO_2^{2+}, Cl^-\right)(m_{UO_2^{2+}})(m_{Cl^-})\ln 10 \\ &+ \epsilon\left(UO_2Cl^+, Cl^-\right)(m_{UO_2Cl^+})(m_{Cl^-})\ln 10 = -\frac{2A\ln 10}{(1.5)^3}\left(t - 2\ln t - \frac{1}{t}\right) \\ &+ \epsilon\left(UO_2^{2+}, Cl^-\right)m^2\alpha(1+\alpha)\ln 10 + \epsilon\left(UO_2Cl^+, Cl^-\right)m^2(1-\alpha^2)\ln 10.\end{aligned} \tag{27}$$

The extended form of Eq. 25 for calculating ϕ in this case is

$$\phi = \frac{2+\alpha}{3} - \frac{2A\ln 10}{3m(1.5)^3}\left(t - 2\ln t - \frac{1}{t}\right) + \frac{m\ln 10}{3}\epsilon\left(UO_2^{2+}, Cl^-\right)\alpha(1+\alpha) + \frac{m\ln 10}{3}\epsilon\left(UO_2Cl^+, Cl^-\right)(1-\alpha^2). \quad (28)$$

How to use these relations to evaluate the "true" value of the SIT coefficients $\epsilon\left(UO_2^{2+}, Cl^-\right)$ and $\epsilon\left(UO_2Cl^+, Cl^-\right)$? First, we note that the value of $\log_{10}\beta_1^0 = (0.17 \pm 0.02)$ for UO_2Cl^+ was recommended in a recent update on thermodynamic properties of U, Np, Pu, Am and Tc [10]. As discussed above, only the lower bound is available for $\epsilon\left(UO_2^{2+}, Cl^-\right)$, specifying that $\epsilon\left(UO_2^{2+}, Cl^-\right) > 0.21$. In this case, the following algorithm can be used:

(1) One selects the set of values of $\epsilon\left(UO_2^{2+}, Cl^-\right) > 0.21$. For each $\epsilon\left(UO_2^{2+}, Cl^-\right)$ a range of $\epsilon\left(UO_2Cl^+, Cl^-\right)$ is used to solve Eq. 24 with the fixed $\log_{10}\beta_1^0 = (0.17 \pm 0.02)$ for uranyl chloride molalities from 0.1 to 1.4 mol·kg^{-1}, calculating for each molality the value of α, the share of free UO_2^{2+};

(2) At the running value of $\epsilon\left(UO_2^{2+}, Cl^-\right)$, for the range of $\epsilon\left(UO_2Cl^+, Cl^-\right)$ under consideration one calculates $\log_{10}\gamma_\pm$, logarithms of the stoichiometric mean ionic activity coefficients of UO_2Cl_2, see Eq. 23, using the calculated results for α, which are specific for each pair of $\epsilon\left(UO_2^{2+}, Cl^-\right)$ and $\epsilon\left(UO_2Cl^+, Cl^-\right)$. The next step is to find the sum of squared errors, SSE(γ),

$$\mathrm{SSE}(\gamma) = \sum_{i=1}^{N} (\ln 10)^2 \left(\log_{10}\gamma_{\pm,\mathrm{exp}} - \log_{10}\gamma_{\pm,\mathrm{calc}}\right)^2, \quad (29)$$

where N is the number of UO_2Cl_2 molalities under consideration, $\gamma_{\pm,\mathrm{exp}}$ and $\gamma_{\pm,\mathrm{calc}}$ are experimental [12] and calculated with Eq. 23 values of $\gamma_\pm$.

(3) Repeat this procedure for a number of $\epsilon\left(UO_2^{2+}, Cl^-\right)$ and $\epsilon\left(UO_2Cl^+, Cl^-\right)$ values to find results that provide the best agreement (the minimum of SSE) with experimental data on the mean ionic stoichiometric activity coefficients of UO_2Cl_2.

A similar procedure should be employed if osmotic coefficients are used as a source of information, calculating for each pair of $\epsilon\left(UO_2^{2+}, Cl^-\right)$ and $\epsilon\left(UO_2Cl^+, Cl^-\right)$ the value of ϕ with Eq. 28 and finding the minimum of the function SSE(ϕ), given by

$$\mathrm{SSE}(\phi) = \sum_{i=1}^{N} \left(\phi_{\mathrm{exp}} - \phi_{\mathrm{calc}}\right)^2. \quad (30)$$

3.1.3 Thermodynamic Activities of Components of the Binary System UO_2Cl_2–H_2O

The principial source of data are osmotic coefficients measured in 1951 by Robinson and Lim [26] using $CaCl_2$ as a reference, the same ϕ values are repeated in the monograph of Robinson and Stokes [12]. The values of activity coefficients of UO_2Cl_2 solutions are obtained by the Gibbs–Duhem integration of ϕ results. The uncertainty of ϕ data is estimated in the current study to be ~0.005 (~0.5%) using the reported isopiestic molalities of UO_2Cl_2 and $CaCl_2$ and employing the current [30] recommendations of osmotic coefficients of calcium chloride solutions. As for the activity coefficients, we note that $\gamma_\pm$ tabulated in [12] are about 1% lower than $\gamma_\pm$ tabulated in [26], although both sets of data are based on the Gibbs–Duhem integration of identical ϕ data. The reason is the lack of ϕ data

Table 1 Values of $\epsilon\left(UO_2Cl^+, Cl^-\right)$ corresponding to the minimum of SSE at given $\epsilon\left(UO_2^{2+}, Cl^-\right)$ around the absolute minimum ofSSE

$\epsilon\left(UO_2^{2+}, Cl^-\right)$	$\epsilon\left(UO_2Cl^+, Cl^-\right)$	1000 · SSE
0.29	0.33	11.17
0.30	0.33	8.555
0.304	0.324	7.727
0.307	0.322	7.336
0.310	0.20	7.043
0.312	0.319	6.898
0.314	0.318	6.797
0.315	0.317	6.762
0.316	0.317	6.740
0.317	**0.316**	**6.7228**
0.318	0.315	6.7230
0.319	0.315	6.726
0.320	0.314	6.744
0.33	0.31	7.485
0.34	0.30	9.498
0.35	0.30	11.78

between 0.1 mol·kg^{-1} and infinite dilution, that makes calculation of $\gamma_\pm$ somewhat uncertain. In any case, we expect that the real uncertainties of $\gamma_\pm$ are not more than 1.5–2%.

As the primary activity data are osmotic coefficients, it would appear logical to minimize the SSE(ϕ) function to evaluate $\left(UO_2^{2+}, Cl^-\right)$ and $\epsilon\left(UO_2Cl^+, Cl^-\right)$. Such preliminary attempts resulted in a very good reproduction of ϕ values, with $\sigma(\phi) = 0.006$. However, $\sigma\left(\ln\gamma_\pm\right) = 0.043$, and calculated mean ionic activity coefficients are systematically lower, by up to 5%, than values tabulated by Robinson and Stokes [12]. Such a difference significantly exceeds the expected uncertainty of $\gamma_\pm$ results. On the other hand, the minimization of the SSE(γ) function gives $\sigma\left(\ln\gamma_\pm\right) = 0.015$ and $\sigma(\phi) = 0.015$, being satisfactory for both sets of activity data. Nevertheless, for this system activity coefficients are the secondary source of data, with accuracy by 3–4 times lower than that of osmotic coefficients. It could be that the reason for such a bias is the fact that the SIT is coarser than the data it should fit. Indeed, the internal precision of the SIT model for reproduction of the activity or osmotic coefficients values is about 3–6%, while the accuracy of γ and ϕ is often better than 0.5%. After several trials, it was decided to minimize the combined function

$$\mathrm{SSE} = 2 \cdot \mathrm{SSE}(\phi) + \mathrm{SSE}(\gamma), \tag{31}$$

which, on one hand, gives a larger weight to primary ϕ data, and, on the other hand, prevents a strong disagreement with results.

3.1.4 Results for Uranyl Chloride

Calculations were performed using the stoichiometric osmotic coefficients, ϕ, and the mean ionic stoichiometric activity coefficients, $\gamma_\pm$, tabulated [12] at 12 molalities of UO_2Cl_2 (m=0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4 mol kg^{-1}). The procedure employed was outlined at the end of Sect. 3.1.2 and implemented as follows: for example, for a value of $\epsilon\left(UO_2^{2+}, Cl^-\right)$= 0.30, the range of $\epsilon\left(UO_2Cl^+, Cl^-\right)$ values from 0.25 to 0.40 was used to 1). solve Eq. 24 relative to α; 2). calculate $\log_{10}\gamma_\pm$ with Eq. 23 and ϕ with

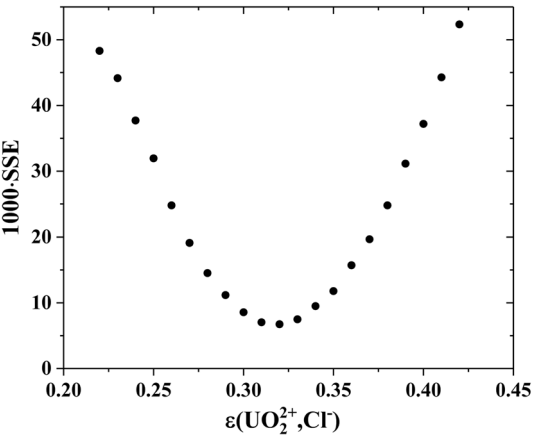


Fig. 1 Values of SSE at various $\epsilon\left(UO_2^{2+}, Cl^-\right)$

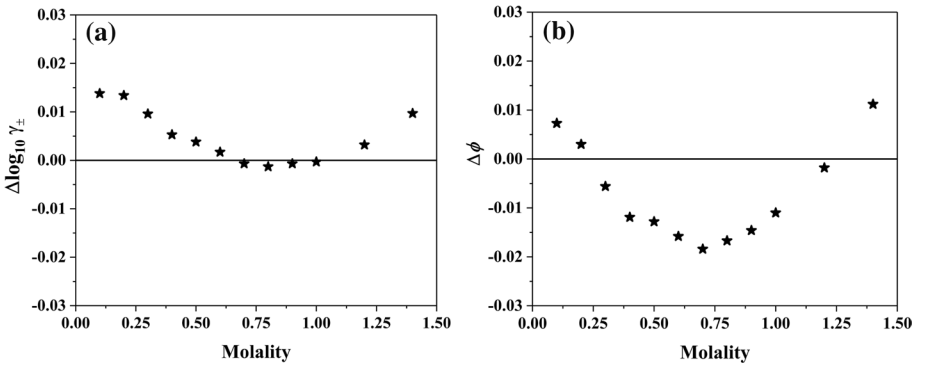


Fig. 2 Deviations of the experimental and fitted values of $\log_{10}\gamma_{\pm}$ (a) and ϕ (b) of UO_2Cl_2

Eq. 28. After that for each pair $\epsilon\left(UO_2^{2+}, Cl^-\right)$ and $\epsilon\left(UO_2Cl^+, Cl^-\right)$ we calculated the corresponding value of SSE, given by Eq. 31. Values of SSE change regularly, passing through a minimum at $\epsilon\left(UO_2Cl^+, Cl^-\right) = 0.33$. The corresponding point ($\epsilon\left(UO_2^{2+}, Cl^-\right)$, SSE) is given in Table 1; Fig. 1. Repeating the same procedure for a large set of $\epsilon\left(UO_2^{2+}, Cl^-\right)$ and $\epsilon\left(UO_2Cl^+, Cl^-\right)$ values, we found that the global minimum of SSE is located at $\epsilon\left(UO_2^{2+}, Cl^-\right)= 0.317$ and $\epsilon\left(UO_2Cl^+, Cl^-\right) = 0.316$. Obtained results are presented in Fig. 1 and in Table 1 (only values around the global minimum of SSE). The $\epsilon\left(UO_2^{2+}, Cl^-\right)$ and $\epsilon\left(UO_2Cl^+, Cl^-\right)$ results, corresponding to the absolute minimum of the SSE function, are given in Table 1 in bold.

The deviations of the experimental [12] mean ionic stoichiometric activity coefficients, $\gamma_{\pm}$, and the stoichiometric osmotic coefficients, ϕ, from the corresponding values, calculated with $\log_{10}\beta_1^0 = 0.17$, $\epsilon\left(UO_2^{2+}, Cl^-\right) = 0.317$ and $\epsilon\left(UO_2Cl^+, Cl^-\right) = 0.316$, using Eqs. 23 and 28, are shown in Fig. 2a,b. The uncertainty $\sigma(\ln\gamma_{\pm})$ for the reproduction of 12 $\gamma_{\pm}$ data points is 0.017 (the maximum error in $\gamma_{\pm}$ is 3.2%), and the uncertainty $\sigma(\phi)$ for 12 ϕ data points is 0.013 (the maximum deviation is 0.018). The deviations are non-random.

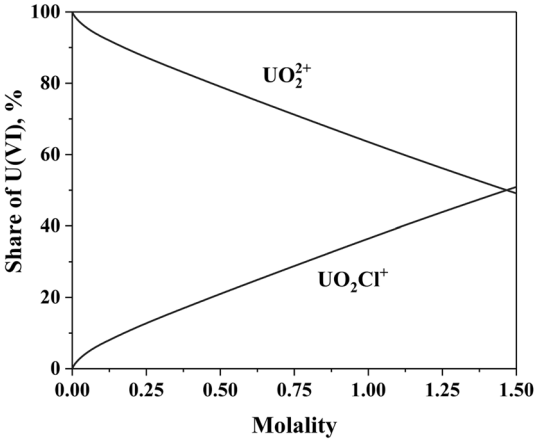


Fig. 3 Calculated speciation of U(VI) in UO_2Cl_2 solutions

The reason for such a non-random distribution of deviations is a poor internal accuracy of the SIT model (about 3–6%) in comparison with accuracy of $\gamma_{\pm}$ (< 2%) and ϕ (~ 0.005).

The calculated speciation of uranyl ion in UO_2Cl_2 solutions is shown in Fig. 3. The uncertainty of α, the share of uncomplexed UO_2^{2+}, increases with UO_2Cl_2 concentration up to about 15%, when counting all contributions due to uncertainties of $\log_{10}\beta_1^0$, $\epsilon\left(UO_2^{2+}, Cl^-\right)$ and $\epsilon\left(UO_2Cl^+, Cl^-\right)$.

We estimate the uncertainties of $\epsilon\left(UO_2^{2+}, Cl^-\right)$ to be ± 0.03 and $\epsilon\left(UO_2Cl^+, Cl^-\right)$ to be ± 0.02: $\epsilon\left(UO_2^{2+}, Cl^-\right) = (0.32 \pm 0.03)$ and $\epsilon\left(UO_2Cl^+, Cl^-\right) = (0.32 \pm 0.02)$. Within these limits, $\sigma(\ln\gamma_{\pm}) \leq 0.05$ and $\sigma(\phi) \leq 0.04$. If the range of UO_2Cl_2 molalities used for determination of the SIT coefficients is increased to 2.0 mol·kg^{-1}, then the optimal values are $\epsilon\left(UO_2^{2+}, Cl^-\right) = 0.30$ and $\epsilon\left(UO_2Cl^+, Cl^-\right) = 0.34$, i.e., the effect is modest and within the indicated uncertainties. The stronger effect has the change of β_1^0 values. As discussed in a current update on thermodynamic properties of uranium compounds [10], recent results [33] are consistent with $\log_{10}\beta_1^0 = 0.0$ for reaction 12. When repeating the same procedure of the SIT coefficients determination with $\log_{10}\beta_1^0 = 0.0$, we obtain $\epsilon\left(UO_2^{2+}, Cl^-\right) = 0.29$ and $\epsilon\left(UO_2Cl^+, Cl^-\right) = 0.28$. It means, that β_1^0 and the SIT coefficients for partially associated electrolytes are strongly correlated and, if the recommendations for β_1^0 are changed, then $\epsilon\left(UO_2^{2+}, Cl^-\right)$ and $\epsilon\left(UO_2Cl^+, Cl^-\right)$ should be recalculated.

3.2 The case of Uranyl Nitrate

3.2.1 Nitrate Complex Formation in $UO_2(NO_3)_2$ Solutions

EXAFS data [34] are consistent with the formation of several nitrate complexes of uranyl ion in aqueous solutions, up to a complex with three coordinated nitrate ions. In those runs, the total U(VI) concentration was 0.04 mol·dm^{-3}, and the $[NO_3^-]/[U(VI)]$ ratios exceeded 70. At $c = 2.9$ mol·dm^{-3} of nitrate ion the average NO_3^- coordination was 1.1, growing to 2.5 in 14.5 mol·dm^{-3} NO_3^-, i.e., the notable formation of complexes with two and three coordinated nitrate was observed only at high nitrate concentrations. As in the case of

Table 2 Values of $\epsilon\left(UO_2NO_3^+, NO_3^-\right)$ corresponding to the minimum of SSE at given $\epsilon\left(UO_2^{2+}, NO_3^-\right)$ around the absolute minimum of SSE

$\epsilon\left(UO_2^{2+}, NO_3^-\right)$	$\epsilon\left(UO_2NO_3^+, NO_3^-\right)$	$1000 \cdot SSE$
0.27	0.35	8.375
0.275	0.344	6.713
0.278	0.340	6.263
0.279	0.339	6.208
0.280	**0.338**	**6.200**
0.281	0.337	6.240
0.282	0.336	6.328
0.285	0.333	6.873
0.29	0.33	8.790

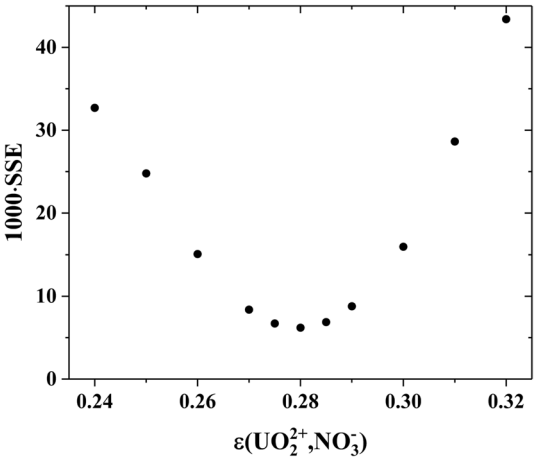


Fig. 4 Values of SSE at various $\epsilon\left(UO_2^{2+}, NO_3^-\right)$

uranyl chloride, we expect that in the binary $UO_2(NO_3)_2$–H_2O system, where the $[NO_3^-]/[UO_2]$ ratio is equal to 2, the average NO_3^- coordination will be smaller, and at $UO_2(NO_3)_2$ molalities below ~2.0 mol·kg^{-1} the first nitrate complex $UO_2NO_3^+$ dominates absolutely.

For the complex formation reaction

$$UO_2^{2+} + NO_3^- \overset{K}{\rightleftharpoons} UO_2NO_3^+, \tag{32}$$

the recent update on thermodynamic properties of uranium [10] recommends $\log_{10}\beta_1^0 = -(0.19 \pm 0.15)$.

3.2.2 Results for Uranyl Nitrate

All relations, discussed for the case of uranyl chloride, Eqs. 13–28, remain valid for uranyl nitrate because the valence type of an electrolyte (2:1) and the stoichiometry of the dominating complex (1:1) are identical to those of uranyl chloride. Again, preliminary calculations have been made minimizing the SSE(ϕ) function. As in the case of uranyl chloride, a good reproduction of ϕ values, with $\sigma(\phi) = 0.005$, was found. However, $\sigma\left(\ln\gamma_{\pm}\right) = 0.037$, and the calculated mean ionic activity coefficients were systematically

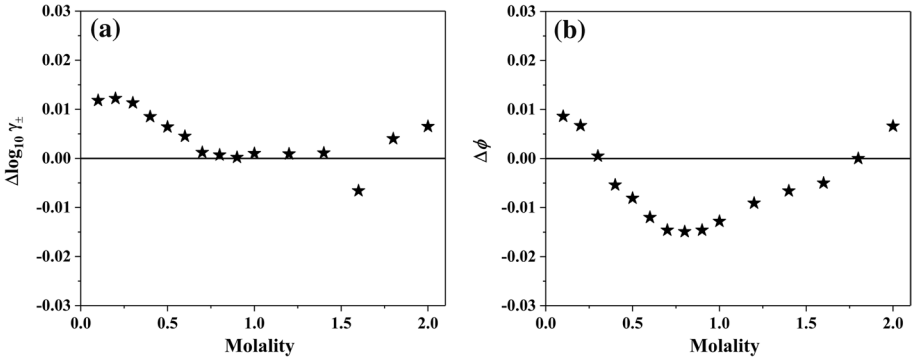


Fig. 5 Deviations of the experimental and fitted values of $\log_{10}\gamma_{\pm}$ (**a**) and ϕ (**b**) of $UO_2(NO_3)_2$

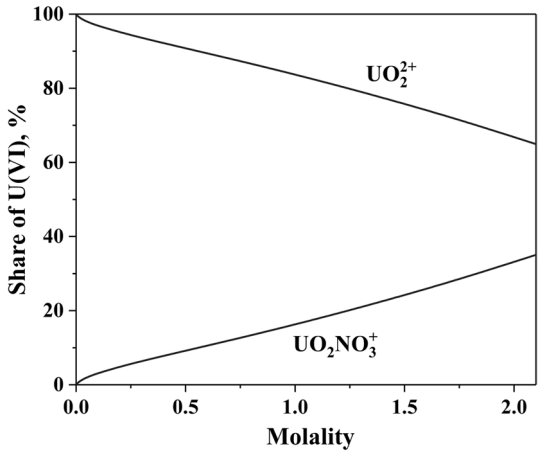


Fig. 6 Calculated speciation of U(VI) in $UO_2(NO_3)_2$ solutions

lower, by up to 4%, than values tabulated by Robinson and Stokes [12]. It was checked that the minimization of the SSE(γ) function gave $\sigma\left(\ln\gamma_{\pm}\right) = 0.015$ and $\sigma(\phi) = 0.014$, being satisfactory for both sets of activity data. Taking into account that the expected accuracy of ϕ values is higher than that of $\gamma_{\pm}$, final calculations again were made minimizing the SSE function, see Eq. 31, thus giving a larger weight to primary ϕ data. Again, we used ϕ and $\gamma_{\pm}$, tabulated [12] at 15 molalities of $UO_2(NO_3)_2$ ($m = 0.1$, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 mol·kg^{-1}). Obtained results are presented in Fig. 4 and in Table 2 (only values around the global minimum of SSE). The $\epsilon\left(UO_2^{2+}, NO_3^-\right)$ and $\epsilon\left(UO_2NO_3^+, NO_3^-\right)$ results, corresponding to the absolute minimum of the SSE function is given in Table 2 in bold.

The deviations of the experimental [12] mean ionic stoichiometric activity coefficients, $\gamma_{\pm}$, and the stoichiometric osmotic coefficients, ϕ, from the corresponding values, calculated with $\log_{10}\beta_1^0 = -0.19$, $\epsilon\left(UO_2^{2+}, NO_3^-\right) = 0.28$ and $\epsilon\left(UO_2NO_3^+, NO_3^-\right) = 0.34$, are shown in Fig. 5a, b. The uncertainty $\sigma(\ln\gamma_{\pm})$ for the reproduction of 15 $\gamma_{\pm}$ data points is 0.016 (the maximum error in $\gamma_{\pm}$ is 1.8%), and the uncertainty $\sigma(\phi)$ for 15 ϕ data points is 0.010 (the maximum deviation is 0.015).

The calculated speciation of the uranyl ion in $UO_2(NO_3)_2$ solutions is shown in Fig. 6. The uncertainty of α, the share of uncomplexed UO_2^{2+}, increases with $UO_2(NO_3)_2$ concentration up to about 25%, mainly due to uncertainty of $\log_{10}\beta_1^0$ (± 0.15).

We estimate the uncertainties of both $\epsilon\left(UO_2^{2+}, NO_3^-\right)$ and $\epsilon\left(UO_2NO_3^+, NO_3^-\right)$ at $\log_{10}\beta_1^0 = -0.19$ to be ± 0.02: $\epsilon\left(UO_2^{2+}, NO_3^-\right) = (0.28 \pm 0.02)$ and $\epsilon\left(UO_2NO_3^+, NO_3^-\right) = (0.34 \pm 0.02)$. Within these limits, $\sigma(\ln\gamma_\pm) \leq 0.06$ and $\sigma(\phi) \leq 0.04$. In the case of uranyl nitrate, the uncertainty of $\log_{10}\beta_1^0$ is relatively large, $\pm$ 0.15 $\log_{10}$ units. For the maximum value of $\log_{10}\beta_1^0 = -0.04$, the optimal values of the SIT coefficients are $\left(UO_2^{2+}, NO_3^-\right) = 0.29$ and $\epsilon\left(UO_2NO_3^+, NO_3^-\right) = 0.36$; for the minimum value of $\log_{10}\beta_1^0 = -0.34$, the optimal values of the SIT coefficients are $\epsilon\left(UO_2^{2+}, NO_3^-\right) = 0.27$ and $\epsilon\left(UO_2NO_3^+, NO_3^-\right) = 0.32$, i.e., within the uncertainty ranges of initially recommended values.

4 Conclusion

The relations from the thermodynamics of associated electrolytes [12, 25], Eqs. 8 and 9 are used as a basis for evaluation of the SIT coefficients for the interactions between the uranyl cation and chloride and nitrate anions. The literature values of the stoichiometric osmotic and mean ionic activity coefficients of UO_2Cl_2 ($0.1 \leq m \leq 1.4$ mol·kg^{-1}) and $UO_2(NO_3)_2$ ($0.1 \leq m \leq 2.0$ mol·kg^{-1}) were employed in the evaluation procedure together with the recommended [10] values of β_1^0 for the stability constants of UO_2Cl^+ and $UO_2NO_3^+$, equal to $\log_{10}\beta_1^0 = (0.17 \pm 0.02)$ and $\log_{10}\beta_1^0 = -(0.19 \pm 0.15)$, correspondingly. Useful byproducts of the calculation procedure are the SIT interaction coefficients for the complex ions. Results are given below:

$\epsilon\left(UO_2^{2+}, Cl^-\right) = (0.32 \pm 0.03)$;

$\epsilon\left(UO_2Cl^+, Cl^-\right) = (0.32 \pm 0.02)$;

$\epsilon\left(UO_2^{2+}, NO_3^-\right) = (0.28 \pm 0.02)$;

$\epsilon\left(UO_2NO_3^+, NO_3^-\right) = (0.34 \pm 0.02)$.

It should be noted that the evaluated SIT interaction coefficients depend relatively strongly on the values of β_1^0 used in the calculation procedure. If the recommendations for β_1^0 are changed, then the SIT interaction coefficients should be recalculated.

As pointed out by an anonymous reviewer, results of this study support a method of estimation of interaction coefficients of metal ion complexes proposed by Ciavatto [35], according to which the value for the first complex of the stoichiometry ML in the XY medium is close to a relation

$$\varepsilon(\mathrm{ML}, \mathrm{XY}) = 1/2[\varepsilon(\mathrm{M,Y}) + \varepsilon(\mathrm{L,X})]. \tag{33}$$

Applying this relation to the first chloride complex of uranyl ion in the UO_2Cl_2 medium, one obtains

$$\epsilon\left(UO_2Cl^+, Cl^-\right) = 1/2\left[\varepsilon(UO_2^{2+}, Cl^-) + \varepsilon(Cl^-, UO_2^{2+})\right] = \varepsilon(UO_2^{2+}, Cl^-) \approx (0.32 \pm 0.03), \tag{34}$$

in an exact agreement with the value obtained in this work (0.32 ± 0.02). For the first nitrate complex of uranyl ion the predicted by Eq. 33 value is $\epsilon\left(UO_2NO_3^+, NO_3^-\right) \approx (0.28 \pm 0.02)$, in a reasonable agreement with our result (0.34 ± 0.02).

The proposed procedure can be easily applied to other partially associated systems, where the mean ionic activity coefficients are determined experimentally and reliable values of β_1^0 are recommended.

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Declarations

Conflict of interest The author declares that he has no competing financial interest.

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